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PREPARATION OF 2-ETHOXY-4-DIETHYLAMINO-
BENZENE-1-DIAZONIUMBOROFLUORIDE

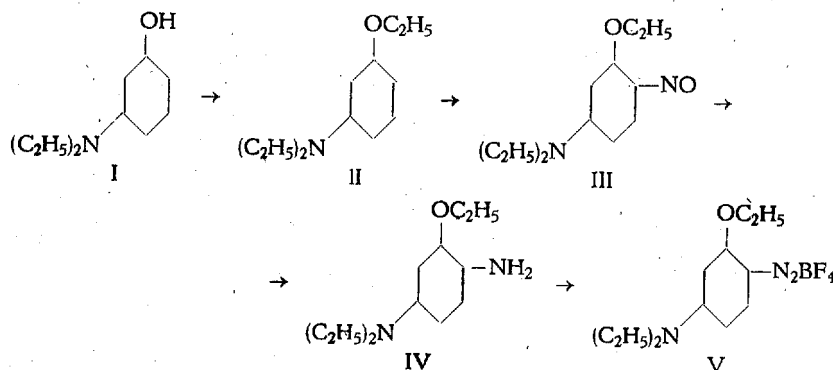
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The preparation of 2-ethoxy-4-diethylaminobenzene-1-diazoniumborofluoride is described. A stable diacetyl derivative is formed by treating 2-ethoxy-4-diethylamino-1-aminobenzene with acetic anhydride.

In the course of preparing materials for an investigation to be carried out within this laboratory we prepared 2-ethoxy-4-diethylaminobenzene-1-diazoniumborofluoride. The product was obtained by the method outlined in the following reaction scheme:



*Reverdin*¹⁾ obtained II by ethylation of m-phenetidine and gives 286° C as the boiling point. We prepared II by ethylation of m-diethylaminophenol (I) with diethyl sulphate and found a boiling point of 268—270° C at atmospheric pressure and of 145° C at a pressure of 14 mm. We repeated the method of *Reverdin* and found again a boiling point of 268° C. The boiling point of II under reduced

¹⁾ F. Reverdin, Bull. soc. chim. France [4] 17, 278 (1915).

pressure is in full agreement with that found by *Brown and Mason*²⁾, who give 148° C at a pressure of 15 mm. Presumably a typographical error has crept into *Reverdin's* paper.

The emerald green nitroso compound III, obtained in good yield, has a melting point of 72.5° C. The amino compound IV, a colourless liquid with a boiling point of 167—169° C at 14 mm, darkens rapidly with oxygen; the stable diacetyl amino compound melts at 81.5° C. The diazonium compound was separated as the borofluoride in fine yellow crystals.

Experimental Section.

1-Ethoxy-3-diethylaminobenzene.

16.5 g (0.1 mole) of diethylaminophenol are dissolved in 40 ml of a 20 % sodium-hydroxide solution and a small quantity of sodium hyposulfite is added to prevent oxidation. When all the diethylaminophenol has been dissolved 16 g of diethyl sulphate is poured in. While stirring and gradually heating up to 60° C the reaction starts and an emulsion is formed. Heating and stirring is then stopped and the mixture is slowly cooled to room temperature. An oily brown liquid separates at the top of the mixture.

Three portions are united and extracted with ether. The etherical solution is dried with sodium sulphate and filtered, the ether then being distilled off. The residue is distilled under reduced pressure and boils at 145°/14 mm. This product distils as a clear, colourless, viscous oil at 268—270° under atmospheric pressure. The yield after both distillations is 35 g (60 %); $n_D^{25} = 1.5325$.

2-Ethoxy-4-diethylamino-1-nitrosobenzene.

35 g (0.18 mole) of ethoxy-diethylaminobenzene are dissolved in 75 ml of 30 % hydrochloric acid. The solution is cooled to 5° C and then 150 g of ice is added, lowering the temperature to -10° C. While stirring a solution of 13.2 g of sodium nitrite in 75 ml water is dropped into the solution in the course of 10 minutes. The colour of the solution turns orange and after about 20 minutes the yellow salt separates. After cooling with ice and salt and continually stirring the product is filtered off after one hour. The compound is dried in a vacuum desiccator for 24 hours and yields 36 g (78 %). A part of the salt is treated with a sodium hydroxide solution and the free base extracted with benzene. After drying and evaporating the benzene an oil resulted which after a few days solidified. The emerald green nitroso compound was recrystallized from a mixture of petrol and benzene. The compound melts at 72.5° C.

Found: C 64.92; H 7.94; N 12.84.

Calc. for $C_{12}H_{18}O_2N_2$ (222.16): C 64.82; H 8.17; N 12.61.

2-Ethoxy-4-diethylamino-1-aminobenzene.

70 g of the hydrochloride of ethoxydiethylaminonitrosobenzene are gradually poured into a hot mixture of 250 ml of a solution of stannous chloride (67 g per 100 ml) and 150 ml of hydrochloric acid (sp.gr. 1.19) while stirring. The contents of the 2 l beaker are then stirred and heated for about 15 minutes. After cooling to

²⁾ W. R. Brown and F. A. Mason. J. Chem. Soc. 1933, 1264.

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room temperature 500 g ice is added and the beaker is filled up to 1500 ml with distilled water, the contents then being made alkaline with a 40 % solution of sodium hydroxide. The liquid is extracted with 500 ml benzene. After drying with anhydrous sodium sulphate the benzene solution is distilled under reduced pressure. The product boiling at 167—169/14 mm is collected. The yield is 41.5 g (73 %); $n_D^{25} = 1.5485$.

The compound was characterized as the diacetyl derivative. It is prepared by boiling the amino compound with an excess of acetic anhydride for 10 minutes. The mixture is then poured into distilled water and boiled for 10 minutes. When cooled to room temperature white crystals separate. After recrystallization twice from alcohol the compound melts at 81.5° C. Analysis proves that the diacetyl derivative is formed.

Found: C 65.82; H 7.97; N 9.77.

Calc. for $C_{16}H_{24}O_3N_2$ (292.21): C 65.71; H 8.28; N 9.59.

2-Ethoxy-4-diethylaminobenzene-1-diazoniumborofluoride.

In a 250 ml beaker 38.8 g of the amino compound are dissolved in a mixture of 100 ml water and 60 ml concentrated hydrochloric acid (sp.gr. 1.19). The solution is cooled with an ice-salt mixture to 0° and then 50 g ice is added. 14 g of sodium nitrite dissolved in 50 ml water is dropped into the solution in the course of about 20 minutes while stirring. After 30 minutes 30 g ammonium borofluoride is added and stirring is continued for 45 minutes. The precipitated diazonium borofluoride is filtered off, washed with alcohol and ether and dried in a vacuum desiccator. The yield of fine yellow crystals amounts to 52 g (90 %).

Eindhoven, April 1952.

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